AN ISOTOPE DILUTION STUDY OF EXCHANGEABLE
OXYGEN IN PREMIUM COAL SAMPLES

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The analysis of the moisture content of coals has been the subject of a number of extensive discussions (1-3).   Interest in the determination of water in coal is a result of both its importance in commerce and its influence on the elemental analysis of the organic portion of the coal. Although simple weight loss methods, such as ASTM 3173, are the accepted methods for the analysis of moisture in coal, it is well documented that these methods are not without error, especially in low-rank coals.   A question of importance is, How much of the water of combustion determined by classical combustion analysis of the coal was present in the "dry" coal as water and is not a combustion product?   This water, if present in "dry" coal, can introduce a significant error into the organic elemental analysis. For example, 1% water present in a dry Illinois #6 coal and mistakenly identified as a product of combustion would introduce an error of ~3% in the hydrogen analysis and ~10% in the oxygen analysis.   The 3% error in the hydrogen analysis translates into an error of 3 H/100 C for the Illinois No. 6 coal.

Our particular concern regarding the accurate determination of water stems from an interest in the chemistry of hydrogen during direct coal liquefaction.   In such systems the change in organic hydrogen across a reactor will often be in the range of 5 H/100 C.   If errors due to the unknown amount of moisture in coal are +3 H/100 C, a problem exists.   If we cannot have confidence in our ability to determine the change in organic elemental composition across a reactor, we cannot, with confidence, discuss the chemistry occurring in that reactor.

The investigation of coal structure can also be complicated by inadequate analysis of the water in the coal.   Drying procedures for moisture determination may cause substantial structural changes and, if done in the presence of oxygen, may also induce significant oxidation.   The problem of structural collapse on drying is more acute for studies of lower rank coals.   Study of the dependence of coal structure on moisture content would be aided by improved methods to measure the nature and amount of water in whole coals.

A difficulty with improving the ability to quantitate water in coal is that truly independent methods do not always exist.   The "true" value of any analytical parameter is always easier to determine if totally independent

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methods exist to determine that parameter. This paper describes the possi-
bility of using a simple isotope dilution technique to determine the water
content of coal and presents a comparison of these isotope dilution measure-
ments with classical results for the set of Argonne coals from the premium
coal sample program (4).

Isotope dilution is a widely used analytical method and has been
applied to the analysis of water in matrices as diverse as chicken fat (4),
living humans (5), and coal (6). Virtually all of these applications
involved the use of deuterium as the diluted isotope. This poses some
problems if the sample contains a significant amount of exchangeable organic
hydrogen and one is interested in discriminating exchangeable organic
hydrogen from water. This is a potential problem in the coal system. To
avoid this potential problem ^{18}O was used as the diluted isotope in this
work.

Experimental

The isotope dilution experiment, as applied in this study, involves
equilibration of a fixed amount of labeled water with a known amount of
coal. If it can be established that complete equilibration has been
achieved and if proper allowance is made for isotopic impurities and contri-
butions from the apparatus, the isotope ratio of the final equilibrated
system directly measures the exchangeable isotope reservoir in the coal.
Further work can then be directed to determining what species compose the
exchangeable oxygen reservoir.

The equilibration of the coal with labeled water is accomplished by
placing a weighed amount of coal (20-300 mg) in a thin-walled Pyrex tube,
adding 5 µL of $H_2^{18}O$, and using a torch to seal the equilibration tube. The
premium coals used were the 100-mesh samples, and all equilibration tubes
were filled and sealed within 15 minutes of opening the ampoule. The $H_2^{18}O$
was 90% enriched and was obtained from Mound Laboratories. Before sealing,
a small amount of dry $CO_2(g)$ is added to each equilibration tube as a probe
molecule to facilitate mass spectrometric analysis of the isotope ratio.
Before analysis, the sealed tubes are equilibrated at 100°C for 16 hours.
Measurement of the equilibration rate of coal samples using this experi-
mental approach established that at 100°C, 16 hours was sufficient to
guarantee complete equilibration. The isotope ratio measurement on the
final system was done by measuring the relative abundances of the isotopic
CO_2 species ($C^{16}O_2$, $C^{16}O^{18}O$, and $C^{18}O_2$) using a CEC 103 mass spectrometer.
Stable isotope geochemists routinely use CO_2 to measure the oxygen isotopic
composition of water samples (7). Distilled water was used for calibration.

Results and Discussion

Determination of the size of the exchangeable oxygen reservoir in the
premium coals was accomplished by plotting the observed $^{16}O/^{18}O$ isotope
ratio against the sample size. Since the amounts of labeled water, CO_2, and
any exchangeable oxygen associated with the sample vessel are held constant,
the change in isotope ratio with sample size should be a function of only
the size of the exchangeable oxygen reservoir in the coal. The isotope
dilution data obtained for the eight currently available premium coals are

presented in Figure 1. The slopes of the plots shown in Figure 1 are simply proportional to the size of the exchangeable oxygen reservoir in each of the premium coals.

Conversion of the raw data to "water" content and comparison of these results with the best currently available moisture analyses on the premium coals is shown in Table 1. The assumption that is made is that the exchangeable oxygen reservoir is all present as water. These results indicate good agreement between the isotope dilution measurement and the classical moisture measurements on this set of samples. There appears to be a small systematic positive difference between the isotope dilution and the weight loss results. This difference is believed to be outside our experimental error. Before the set of premium coals was analyzed, a number of ground coals being used in process-related studies had been analyzed by this method. For these samples, which had not been handled with the care lavished on the premium samples, discrepancies between the isotope dilution measurements and the classical weight loss analyses were significantly greater. This is illustrated by the last two entries in Table 1. At this point in the development of the isotope dilution technique, a definitive explanation of the larger discrepancies between isotope dilution and weight loss results for the non-premium samples would be premature. A potential source of these differences could be mild oxidation and structural changes in the non-premium samples, resulting in water being more strongly bound and thus incompletely measured in the weight loss analyses. Further work is needed to clarify the reasons for these differences.

The data presented indicate that an isotope dilution approach is capable of reproducibly measuring the size of an exchangeable oxygen reservoir in coal. To determine what oxygen is included in the exchangeable oxygen reservoir, the size of the reservoir was determined for a variety of model systems, including clay minerals, calcite, gypsum, inorganic hydrates, phenolics, carboxylic acids, carboxylate salts, carboxylate salt hydrates, and accepted geochemical standards. The discussion of all these results exceeds the scope of this preprint; however, the preliminary conclusion is that under the conditions described in this work, the exchangeable oxygen reservoir includes most strongly bound hydrate water in both organic and inorganic systems and does not include any organic oxygen in compounds that are stable under the equilibration conditions.

Conclusions

Equilibrium isotope exchange for the investigation of oxygen in coal appears to have promise as a tool for determination of the "true" water content of coals. Its applicability appears to extend across the rank scale. The technique measures the size of the exchangeable oxygen reservoir under very mild conditions without removing the water from the coal, thus avoiding structural changes that could complicate the analysis. A more comprehensive discussion of the results on a variety of systems is currently being prepared. Preliminary results indicate that it may provide a simple, reliable, and totally independent method for the measurement of coal water content. Comparison of this method with classical weight loss methods may provide a significant improvement in our ability to measure the "true" water content of coal and thus the "true" organic hydrogen and oxygen contents as well.

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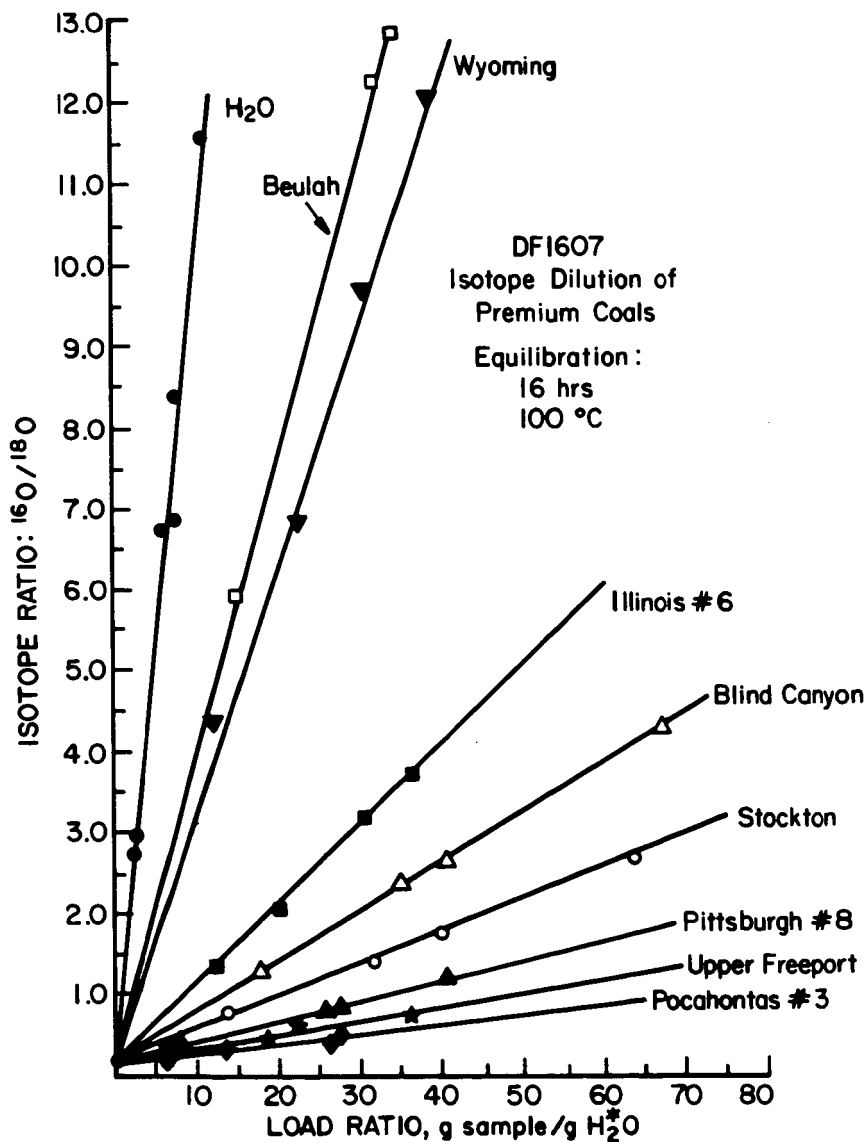   224.

Figure 1. Isotope Dilution Analysis of Premium Coals.

NO./13,806

TABLE 1.
"MOISTURE" IN COALS
(Exchangeable Oxygen Reservoir)

Coal	Isotope Dilution Analysis (Wt%)	Standard Method (Wt%)*	
Beulah-Zap	34.4	32.8	
Wyodak	30.0	28.84	
Illinois #6	9.6	8.8	
Blind Canyon	5.9	4.7	"Premium" Samples
Stockton	3.9	2.6	
Pittsburgh #8	2.5	1.8	
Upper Freeport	1.5	0.83	
Pocahontas	1.0	0.66	
Clovis Point	27.6	20.4	"Non-Premium" Samples
River King	9.8	7.7	

*For Premium Samples, Data Obtained from Argonne National Lab.
Non-Premium Samples Were Analyzed by ASTM 3173.